

STORAGE STABILITY OF FUELS - IDENTIFICATION OF NITROGEN COMPOUNDS AND THEIR EVOLUTION DURING AGEING IN ABSENCE AND PRESENCE OF ADDITIVES by M. Dorbon, C. Bernasconi*, J. Gaillard, J. Denis, Institut Francais du Petrole, FRANCE and *ELF FRANCE, Centre de Recherche de Solaize, FRANCE

INTRODUCTION

The growing need for Diesel fuels and developments in refining processes, particularly the increased use of Fluid Catalytic Cracking (FCC), have led refiners to consider introducing Light Cycle Oils (LCOs) in formulations of distillates for home-heating oils and Diesel fuels.

Unfortunately, the cracking products often undergo changes, and induce darkening and the formation of insolubles liable to cause difficulties in use.

The degradation mechanisms have not yet been clearly identified despite many interesting investigations already conducted. Taylor and Frankenfeld¹ reviewed a number of hypotheses and conclusions drawn from previous studies, and stressed the determining role of oxidation. Many articles have suggested that carboxylic, phenolic and sulfonic acids produced by the oxidation of middle distillates exert a catalytic effect on fuel instability^{2, 3, 4} and on the quantity of sediments formed⁴. Bhan *et al*⁵ demonstrated that aromatic compounds and non-basic nitrogen compounds, could be the main source of sediment formation. Recently, Pedley *et al*^{6, 7} found that a major source of strongly-colored sediments was the oxidation of phenalene to phenalenone, followed by the reaction of phenalenone with alkyl indoles, yielding addition products that precipitate under the influence of sulfonic acids, themselves produced by the oxidation of thiols.

In previous work⁸ we found that most of the changing compounds were located in the heaviest distillation fraction of LCO (BP > 310 to 315 °C) and that better stability could be achieved by removing this fraction.

Among these compounds, those containing nitrogen were largely identified⁹, showing that LCOs always contain three clearly distinct main groups of nitrogen compounds: anilines, alkyl indoles and alkyl carbazoles, and that only the alkyl indoles are subject to change during degradation in storage.

This identification led to the development of a method for determining the changes in alkyl indoles during the storage of several mixtures of straight-run distillates and LCOs in the absence and presence of additives.

EXPERIMENTAL

Several middle distillates were employed and several additives were tested for this investigation.

Middle distillates

- | | |
|---------------------------------------|---------------|
| •Three straight-run distillates (SR): | B1 and C1, E1 |
| •Three low-sulfur LCOs: | B2 and C2, D2 |
| •Three high-sulfur LCOs: | B3 and C3, D3 |

The properties of these materials are listed in Table 1. All the ageing tests were performed on LCOs and mixtures in 70/30 proportions of SR distillate and LCO. The sulfur content for some of them was accordingly higher than the present French specification of 0.3% S, but this makes the alteration effect of LCOs more pronounced.

Additives

- AD1 and AD2, mixtures of tertiary amines and metal deactivator.
- AD3, multi-purpose additive containing tertiary amines, metal deactivator and dispersant.

These additives were used mainly at 40 and 200 ppm by weight.

Ageing test methods

Three ageing test methods were employed in the laboratory.

- A highly-accelerated method, in which 350 ml of mixture is subjected for 2 h at 120 °C to a stream of 3 l/h of pure oxygen. The apparatus and bottles used are similar to those of method ASTM D-2274. The insolubles are determined by filtration through a 0.8 µm porosity cellulose acetate filter (Millipore filter AA).

The amounts of insolubles adhering to the tube walls after only 2 h were too small to be recovered.

- A similar method to ASTM D-4625, in which 300 ml of mixture is placed in contact with atmospheric air in glass bottles at 43 °C for 12 weeks. The filtrable and adhering insolubles are determined as in ASTM D-4625, except that 0.8 µm cellulose acetate filters are used instead of 1.5 µm glass fibers filters.
- A method corresponding to conditions approaching reality, in glass bottles for one year at room temperature in air. Filtrable and adhering insolubles are determined as above.

For these three methods, the color determinations of new and aged samples were performed according to ASTM D-1500.

These three methods can be considered as complementary owing to the different operating temperatures and atmospheres.

Method for analyzing nitrogen compounds

The selective detection of nitrogen compounds by gas-phase chromatography was performed using a Perkin Elmer 8500 chromatograph equipped with a thermo-ionic detector (NPD) and a packed column injector, modified for megabore capillary columns. The column was a 15 m x 530 µm i.d. fused silica capillary column, coated with a non-polar methyl silicon phase. The temperatures were programmed as follows: from 60 to 160 °C at 2.5 °C·min⁻¹, and from 160 to 200 °C at 2 °C·min⁻¹.

RESULTS AND DISCUSSION

Ageing of middle distillates in the absence of additives

Several straight-run middle distillates and low- and high-sulfur LCOs and mixtures of SR distillates and LCOs (70/30) were subjected to the three ageing tests in the laboratory. Table 2 shows the results in colors and weights of insolubles obtained by these tests.

- It appears that the straight-run middle distillates as such are stable, except in color, irrespective of the operating conditions, temperature and duration.
- Pure LCOs, however, are very unstable over long periods at low temperature, particularly high-sulfur LCOs. Most of the insolubles are found in the form of sediments adhering to the bottle walls.

In short-term tests at high temperature, stability appears to be satisfactory.

- Mixtures of straight-run distillates and LCOs display stability that depends on both of the components. Mixtures based on B1 display greater changes than those based on C1. For B1, the weights of insolubles are higher than anticipated from the results obtained on the two pure components. Filtrable insolubles are present in larger quantities than adhering insolubles. These two remarks do not apply to mixtures based on SR distillate C1. As to the influence of LCOs, as anticipated, mixtures containing low-sulfur LCOs are more stable than those containing high-sulfur LCOs.

If the methods are compared, it appears that the twelve-week method at 43 °C in air is very closely correlated with storage at room temperature. The two-hour method at 120°C in oxygen appears less severe.

Ageing of middle distillates in the presence of additives

Three types of additive, in concentrations of 40 and 200 ppm, were added to the SR distillates/LCOs mixtures B1/B3, C1/C2 and C1/C3, and aged by the three laboratory methods. Table 3 shows the results in color and weight of filtrable and adhering sediments. As a rule, the additives are ineffective against a color change. From the standpoint of sediments, the first two additives AD1 and AD2, based on aliphatic or cyclo-aliphatic tertiary amines combined with a metal deactivator, appear to be more effective according to the accelerated method at 120 °C than with the long-term storage methods at low temperature. The increase in concentration from 40 to 200 ppm does not improve a lot effectiveness according to these tests. Additive AD3, which also contains a dispersant, is more effective in the long-term test, and the concentration effect is significant.

The distribution of the sediments also differs in the long-term tests. With AD1 and AD2, adhering insolubles are higher than filtrable insolubles, and vice versa with AD3. The dispersant component of AD3 tends to keep the insolubles in suspension.

Analysis of ageing as a function of time

To gain a better understanding of the mechanisms of sediment formation and additive action in middle distillates during the different accelerated and long term ageing methods, a kinetic analysis was performed on several SR distillates, LCOs and SR/LCO mixtures (70/30) in the absence and presence of additives.

- Test at 120°C

For this kinetic analysis, two mixtures B1/B2 (70/30) and B1/B3 (70/30) alone and with 40 ppm of AD1 additive were subjected to ageing testing in oxygen for times ranging up to 40 hours (figure 1). A large amount of insolubles is formed during the first few hours, and the increase is then slower. The effectiveness of additive AD1 is substantial, especially during the first hours of rapid change, and then declines but still remains high :

- Tests at 43°C in the absence of additives

Figure 2 shows the curves obtained for constituents and mixtures in 12 weeks tests at 43°C. These curves have various configurations :

- SR distillates C1 and E1 have almost linear increases in insolubles content.
- LCOs give curves with varying configurations. For C2 and C3, a short induction period appears, followed by an abrupt increase in insolubles weight; whereas for D2 and D3, the increase is gradual and stabilization occurs after 8 weeks . Note the difference in scale between low sulfur LCOs and high sulfur LCOs.
- SR distillate / LCO mixtures have highly varying curve configurations as well.
- Tests at 43°C in the presence of additives

Figure 3 shows the curves obtained for SR distillate/LCO mixtures (70/30) in the absence and presence of additives. Additives diminish the amounts of insolubles formed without changing the general configuration of the curves, but preventing the formation of insolubles from reaching too high values.

Changes in nitrogen compounds: analytical method

An analytical procedure was previously developed to identify the nitrogen compounds in LCOs⁹. The same nitrogen compounds were found in many LCOs: aniline and alkyl anilines from C1 to C4, indole and alkyl indoles from C1 to C4, carbazole and alkyl carbazoles from C1 to C3 (Figure 4). Very few differences were observed in the relative proportions of each compound.

The principle of the method is the selective extraction of the nitrogen compounds by liquid chromatography and the analysis of the nitrogen extracts by coupling gas-phase chromatography with mass spectrometry (GC/MS), and by gas-phase chromatography with a specific thermo-ionic detector of nitrogen compounds⁹.

Due to the similarity of composition of the LCOs, it is unnecessary to extract the nitrogen compounds from each sample analyzed. To monitor the changes, these clearly identified compounds are analyzed by gas-phase chromatography with nitrogen specific thermo-ionic detector.

This analytical method can only be qualitative for the following reasons.

- (a) The response of each compound to the detector depends chiefly on the number of nitrogen atoms in the molecule, and also on the type of compound. Owing to the absence of pure compounds, it is impossible to determine the response factor of each compound.
- (b) The proportion of each of these compounds is close to the detection limit, leading to difficulties of integration.

However, the method serves to compare the relative amounts of each nitrogen compound, either between different samples, or between the same samples before and after ageing.

It was previously demonstrated that most of the alkyl indole peaks drop sharply during ageing, whereas the alkyl carbazoles are relatively unaffected (Figure 5). Carbazole in particular was found in the LCOs one of the most important and one of the least altered compounds during storage. This was confirmed by an outside calibration: the height of the carbazole peak remains constant within the experimental errors, for new and aged samples. Hence it proved convenient to use the carbazole in the LCOs as an internal standard. To compare the changes in the alkyl indoles, the ratios of the carbazole/alkyl indole peak heights were determined in different ageing tests, for example as a function of storage time.

Among the 24 alkyl indole peaks counted from 15 to 38 in Figure 4, the eight highest were selected to monitor the changes in these carbazole/alkyl indole peak height ratios. These peaks were:

- 15 and 17 methyl indoles or C1 indoles,
- 19 and 21 C2 indoles,
- 26, 27, 28, 29 C3 indoles.

To assess the significance of this method, a number of repeatability tests were performed on three new and aged C1/C3 samples by successive injections or at intervals of a few days.

Table 4 gives the results of this study.

Changes in the nitrogen compounds observed by gas-phase chromatography analyses were monitored in the following two studies:

- degradation kinetics in ageing tests for LCOs, and for straight-run distillate/LCO mixtures,
- the influence of multi-purpose additives on the ageing degradation of mixtures of straight-run distillates and LCOs.

Effect of test duration on changes in nitrogen compounds

The following products were subjected to ageing:

- LCOs: low-sulfur B2 and high-sulfur C3,
- SR distillate B1/LCO B2 mixture (70/30), and SR distillate B1/LCO C3 mixture (70/30).

The following ageings were carried out:

- at 120 °C in oxygen up to 8 h,
- at 43 °C in air up to 12 weeks.

The results in carbazole/alkyl indole ratios as a function of time are given in Figures 6a, 6b, 6c and 6d for the four products aged at 120 °C. An increase in this ratio can be observed, namely a progressive decrease in the alkyl indole peaks, particularly the C1 and C2 indoles and two of the C3 indoles (26 and 28). This tendency is similar for the four products. As an example, Figure 5 shows a comparison between the NPD chromatograms of LCO B2 before and after ageings. The indole itself (peak 11) also decreases very substantially, but the height of this peak is very difficult to measure in most of the chromatograms, and the corresponding values could not be plotted on the diagrams.

At 43 °C in air, for the same four products, the changes in the nitrogen compounds shown in Figures 7a, 7b, 7c and 7d are similar to those observed at high temperature.

It is interesting to observe that a comparison of these results relative to the decrease in alkyl indoles shows that substantially equivalent values in weights of insolubles are obtained in three months at 43 °C and in 5 to 10 h at 120 °C. This confirms the relationship that may exist between the reactivity of the alkyl indoles and the storage instability of LCOs alone and in mixtures.

Effect of multi-purpose additives on the reactivity of alkyl indoles

Multi-purpose additives AD1, AD2 and AD3 were added at the rate of 40 and/or 200 ppm to the three distillate/LCO mixtures:

- SR distillate B1/ high-sulfur LCO B3 (70/30),
- SR distillate C1/ high-sulfur LCO C3 (70/30),
- SR distillate C1/ low-sulfur LCO C2 (70/30).

These mixtures were subjected to the following ageing tests :

- at 120 °C in oxygen for 2 h,
- at room temperature in air for 12 months.

In addition to the gravimetric determinations performed after filtration of the insolubles (Table 3), the nitrogen compounds were analyzed to monitor their changes.

For the comparative tests performed at 43 °C in 12 weeks, the weights of insolubles are shown in Table 3, but the nitrogen compounds were not analyzed.

Effect on B1/B3 mixtures:

The results are shown in Figures 8a and 8b in the form of the same diagrams as for the previous study, in ratios of carbazole/alkyl indole peak heights for the eight highest peaks.

In the absence of additive, the variation in these ratios or the decrease in alkyl indoles are more pronounced at 120 °C than at room temperature, whereas the weights of insolubles are higher at room temperature than at 120 °C.

Additives AD1, AD2 and AD3 are effective in preventing the reaction of alkyl indoles, because, for all the peaks, they return the carbazole/alkyl indole ratios to values close to the initial values before ageing. This is especially valid for AD1 at 120 °C and at room temperature, and for AD3 at room temperature, whereas the weights of insolubles remain relatively high despite the presence of these additives at room temperature particularly.

Effect on C1/C3 mixtures:

Similar results are shown in Figures 9a and 9b for these mixtures.

The diagrams have the same pattern as the foregoing: increase in the peak ratios, hence decrease in alkyl indoles when ageing without additive, but maintenance of peak ratios at intermediate values or close to the initial values for ageings in the presence of additives. Additive AD1 is more effective for the test at 120 °C than for the test at room temperature, while additive AD3 is highly effective in both types of test. At 40 ppm, and, above all, at 200 ppm, the alkyl indole peaks practically return to their initial value.

For all these C1/C3 mixtures, the weights of insolubles are too low at 120 °C to compare the effect of the additives from this standpoint. At room temperature, however, the weights of insolubles still remain high in the presence of additives, as for the B1/B3 mixtures.

Effect on C1/C2 mixtures:

For C1/C2 mixtures, the weights of insolubles are very low, and demonstrate the good storage stability of these products in mixtures. Tests with additives were not performed at 120 °C. The chromatographic analyses show in Figure 10 that the alkyl indoles preserve their initial content in the ageing test in the absence or presence of additives, which agrees with the relationship between the reactivity of the alkyl indoles and the storage stability.

The investigation of the influence of storage time on the behavior of LCOs and distillates containing a certain proportion of LCO revealed a close correlation between the formation of insolubles and the progressive disappearance of alkyl indoles, providing confirmation of the degradation mechanism proposed by Pedley *et al* 6.

According to this mechanism, moreover, the alkyl indoles only react in the presence of other oxidizable compounds. The products that react with alkyl indoles are perhaps absent in this case. This could explain the fact that in C1/C2 the alkyl indoles are present and not reactive.

The influence of additives on this variation in alkyl indole content during ageing is highly significant. On the one hand, they display great effectiveness in preventing the progressive disappearance of alkyl indoles, because chromatography shows that the alkyl indole peaks retain their initial value. On the other, they are less effective in preventing the formation of insolubles. Hence it appears that other products and other mechanisms are also involved in the degradation of LCOs, independent of the alkyl indoles, and that the additives are poorly effective in combating the detrimental effect of these other products.

CONCLUSIONS

This research project follows an analytical study concerning the identification of nitrogen compounds in middle distillates from fluid catalytic cracking (LCOs) ⁹.

The development of a method for monitoring the changes in nitrogen compounds served to observe the progressive decrease in the indole and alkyl indole contents during actual and laboratory storage tests on LCOs and mixtures of uncracked distillates and LCOs.

A comparison between the weights of insolubles determined during storage and the decrease in alkyl indoles confirms the degradation mechanism proposed by Pedley *et al* ⁶, namely the oxidation of phenalene to phenalenone, followed by the reaction of phenalenone with alkyl indoles, yielding precipitates under the influence of sulfonic acids resulting from the oxidation of thiols.

The analyses performed after the ageing tests conducted in the presence of additives showed that the alkyl indoles retain their initial value, while insolubles are still being formed. This would tend to show that some insolubles could be formed by mechanisms different from the one involving alkyl indoles.

REFERENCES :

- (1) TAYLOR W.F., FRANKENFELD J.W., 2nd. International Conference on Long Term Storage Stabilities of Liquid Fuels, 1986, San Antonio (TEXAS, USA) pp. 456-511.
- (2) HAZLETT R.N., KELSO G., 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels, pp. 541-555
- (3) HILEY R.W. , PEDLEY J.F., Fuel, 1988, vol 67, pp. 469-473.
- (4) HAZLETT R.N., POWER A.J., 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels, 1986, San Antonio (TEXAS, USA), pp. 556-569.
- (5) BAHN O.K., BRINKMAN D.W., GREEN J. B., CARLEY B., Fuel, 1987, vol 66, pp. 1200-1214.
- (6) PEDLEY J.F., HILEY R.W., HANCOCK R.A., Fuel, 1988, vol 67 pp. 1124-1130.
- (7) PEDLEY J.F., HILEY R.W., HANCOCK R.A., Fuel, 1989, vol 68 pp. 27-31.
- (8) BERNASCONI C., CHAFFARDON A., CHARLEUX P., DENIS J., GAILLARD J., DURAND J.P., 3 rd International Conference on Stability and Handling of Liquid Fuels", 1988, London (UK), pp. 423-440.
- (9) DORBON M., BERNASCONI C., Fuel, 1989, vol 68 pp. 1067-1074.

TABLE 1

CHARACTERISTICS OF MIDDLE DISTILLATES

| Characteristics | | SR distillates | | | Low-sulfur LCOs | | | High-sulfur LCOs | | |
|----------------------------|--------------------|----------------|--------|--------|--------------------|--------|--------|---------------------|--------|--------|
| | | B1 | C1 | E1 | B2 | C2 | D2 | B3 | C3 | D3 |
| Flash point | °C | 111 | 106 | 102 | 85 | 92 | 71 | 81 | 70 | 72 |
| Cloud point | °C | 7 | -8 | -1 | -10 | -9 | -37 | -10 | -15 | -10 |
| Cold filter plugging point | °C | 6 | -9 | 0 | -15 | -11 | -37 | -23 | -17 | -19 |
| Pour point | °C | 3 | -12 | -3 | -27 | -21 | <-42 | -43 | -24 | -36 |
| Sulfur | % | 0.14 | 0.04 | 0.11 | 0.84 | 0.51 | 0.59 | 2.54 | 1.31 | 1.69 |
| Total nitrogen | ppm | 265 | 10 | 230 | 630 | 670 | 510 | 440 | 590 | 685 |
| Basic nitrogen | ppm | 170 | 7 | 58 | 100 | 75 | 106 | 90 | 99 | 115 |
| Viscosity at 20°C | mm ² /s | 9.4 | 5.41 | 6.53 | 3.79 | 4.56 | 2.94 | 3.53 | 3.59 | 3.89 |
| Density at 15°C | kg/l | 0.8639 | 0.8276 | 0.8438 | 0.9355 | 0.9106 | 0.8996 | 0.9382 | 0.9118 | 0.9262 |
| DISTILLATION | | | | | | | | | | |
| Initial boiling point | °C | 232 | 220 | 200 | 148 | 191 | 150 | 120 | 132 | 138 |
| Final boiling point | °C | 402 | 355 | 358 | 339 | 354 | 311 | 334 | 342 | 344 |
| MASS SPECTROMETRY | | | | | | | | | | |
| Paraffins | % | 27.4 | 41.8 | | 14 | 12.2 | | 10.8 | 11.7 | |
| Naphthenes | % | 43.2 | 40.5 | | 9.2 | 16.8 | | 7.8 | 9.8 | |
| Monoaromatics | % | 7 | 3.7 | | 10.9 | 10.6 | | 11 | 12.1 | |
| Diaromatics | % | 13.9 | 8.2 | | 38.3 | 34.3 | | 38.1 | 37.7 | |
| Triaromatics | % | 6.6 | 4.4 | | 18 | 17.5 | | 13.4 | 14.7 | |
| Benzothiophenes | % | 1.5 | 0.6 | | 6.7 | 5.7 | | 15.8 | 10.7 | |
| Dibenzothiophenes | % | 0.4 | 0.8 | | 2.9 | 2.9 | | 3.1 | 3.3 | |

TABLE 2

STABILITY TESTS OF DISTILLATES PURE AND IN MIXTURES

| Distillates | Initial color (ASTM D1500) | Insolubles before test mg/100 ml | After 2h. 120°C in O ₂ | | After 12 weeks. 43 °C in air | | | | After 1 year at room temperature in air | | | |
|--------------------------|----------------------------------|--|--------------------------------------|--------------------|---------------------------------|------------------------|----------------------|-------------------|--|------------------------|----------------------|-------------------|
| | | | Color | total Insolub.* | Color | Filterable insolub. | Adhering insolub. | Total insolub. | Color | Filterable insolub. | Adhering insolub. | Total insolub. |
| SR middle distillates | | | | | | | | | | | | |
| B1 | 1 | 0.2 | 1.5 | 0.4 | 3.5 | 0.5 | 0 | 0.5 | 2.5 | 0.3 | 0.5 | 0.8 |
| C1 | 0 | nd | 0 | 0.1 | 0.5 | 0 | 0.3 | 0.3 | 0.5 | 0.1 | 1.5 | 1.6 |
| Low-sulfur LCOs | | | | | | | | | | | | |
| B2 | 2.5 | nd | 3.5 | 0.5 | H8 | 2.5 | 20.9 | 23.4 | | | | |
| C2 | 1.5 | nd | 2.5 | 0.1 | 7 | 6.4 | 10 | 16.4 | 6 | 6.9 | 4.7 | 11.6 |
| High-sulfur LCOs | | | | | | | | | | | | |
| B3 | 2 | 0.2 | <3.5 | 0.2 | 7.5 | 0.8 | 37.1 | 37.9 | | | | |
| C3 | 1.5 | nd | 3 | 0.2 | 7.5 | 34.7 | 10.7 | 45.4 | 7.5 | 42.3 | 17.1 | 59.4 |
| 70/30 mixtures | | | | | | | | | | | | |
| B1/B2 | 2 | 0.1 | 6 | 1.6 | 6 | 7.9 | 4.1 | 12 | | | | |
| B1/C2 | 2 | nd | <3.5 | 0.7 | 5.5 | 6.5 | 2.8 | 9.3 | | | | |
| C1/C2 | 1 | 0.1 | 1.5 | 0.1 | 2.5 | 0.4 | 1.4 | 1.8 | 2.5 | 0.2 | 1.7 | 1.9 |
| B1/B3 | 2 | 0.1 | 6.5 | 13.8 | 5.5 | 11.6 | 5.4 | 17 | 5.5 | 12.6 | 4.7 | 17.3 |
| B1/C3 | 2 | 0.2 | 5 | 5 | 5.5 | 3.8 | 5.9 | 9.7 | | | | |
| C1/C3 | 1 | 0.1 | 1.5 | 0.3 | 2.5 | 0.4 | 6.6 | 7 | 3 | 5.8 | 3.7 | 9.5 |

* No adhering insoluble by this method

TABLE 3

**STABILITY TESTS OF MIDDLE DISTILLATES IN MIXTURES
WITH ADDITIVES**

| Distillates + additives | Initial color (ASTM D1500) | Insolubles before test mg/100 ml | After 2h. 120°C in O ₂ | | After 12 weeks. 43 °C in air | | | | After 1 year at room temperature in air | | | |
|-------------------------------|-------------------------------------|--|--------------------------------------|--------------------|---------------------------------|------------------------|----------------------|-------------------|--|------------------------|----------------------|-------------------|
| | | | Color | total insolub.* | Color | Filterable insolub. | Adhering insolub. | Total insolub. | Color | Filterable insolub. | Adhering insolub. | Total insolub. |
| B1/B3 (70/30) | 2 | 0.1 | 6.5 | 13.8 | 5.5 | 11.6 | 5.4 | 17 | 5.5 | 12.6 | 4.7 | 17.3 |
| + AD1 40 ppm | " | " | 5 | 3.1 | 5.5 | 3.8 | 4.2 | 8 | 5.5 | 6.6 | 4.1 | 10.7 |
| + AD1 200 ppm | " | " | nd | nd | 5.5 | 1.6 | 5.4 | 7 | 5.5 | 5.3 | 5.9 | 11.2 |
| + AD2 40 ppm | " | " | 6 | 3.1 | 5.5 | 2.9 | 6.3 | 9.2 | | | | |
| + AD3 40 ppm | " | " | | nd | 7 | 3.8 | 0.7 | 4.5 | | | | |
| + AD3 200 ppm | " | " | | | 7 | 3.8 | 0.7 | 4.5 | 6.5 | 5.1 | 2.5 | 7.6 |
| C1/C2 (70/30) | 1 | 0.1 | 1.5 | 0.1 | 2.5 | 0.4 | 1.4 | 1.8 | 2.5 | 0.2 | 1.7 | 1.9 |
| + AD1 40 ppm | " | " | | nd | 3 | 0.6 | 1.8 | 2.4 | 3 | 0.3 | 2.7 | 3 |
| + AD1 200 ppm | " | " | | | | | | | 3 | 0.5 | 2.1 | 2.6 |
| + AD3 40 ppm | " | " | | nd | 3 | 0.8 | 0.6 | 1.4 | 3 | 0.8 | 0.4 | 1.2 |
| +AD3 200 ppm | " | " | | | | | | | 3 | 0.2 | 1 | 1.2 |
| C1/C3 (70/30) | 1 | 0.1 | 1.5 | 0.3 | 2.5 | 0.4 | 6.6 | 7 | 3 | 5.8 | 3.7 | 9.5 |
| + AD1 40 ppm | " | " | 1.5 | 0.1 | 2.5 | 1.3 | 4.2 | 5.5 | 3 | 0.8 | 7.8 | 8.6 |
| + AD2 40 ppm | " | " | 1.5 | 0.1 | 3 | 3 | 4.9 | 7.9 | | | | |
| + AD3 40 ppm | " | " | 1.5 | 0.2 | 2.5 | 4.9 | 0.8 | 5.7 | 3 | 4.8 | 2.4 | 7.2 |
| + AD3 200 ppm | " | " | 1.5 | 0.2 | | | | | 3 | 2.6 | 1.6 | 4.2 |

*No adhering insoluble by this method

TABLE 4

REPEATABILITY OF DETERMINATIONS OF
CARBAZOLE/ALKYL INDOLE PEAK HEIGHT RATIOS
BY GAS-PHASE CHROMATOGRAPHY

| Sample | Date | Peak 15 | Peak 17 | Peak 19 | Peak 21 | Peak 26 | Peak 27 | Peak 28 | Peak 29 |
|------------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| C1/C3 no aged | 4/14/89 | 0.9 | 0.5 | 0.33 | 0.33 | 0.8 | 0.9 | 0.75 | 0.7 |
| | 4/17/89 | 1.1 | 0.55 | 0.31 | 0.34 | 0.7 | 0.9 | 0.9 | 0.7 |
| C1/C3 aged at 120°C | 4/14/89 | 1.3 | 0.7 | 0.55 | 0.53 | 1 | 0.96 | 1 | 0.85 |
| | 4/17/89 | 1.4 | 0.8 | 0.6 | 0.53 | 0.9 | 0.92 | 1.05 | 0.9 |
| C1/C3 aged with AD2 at 120°C | 4/14/89 | 1.3 | 0.55 | 0.4 | 0.4 | 0.8 | 1.1 | 1.1 | 0.8 |
| | 4/18/89 | 0.95 | 0.55 | 0.35 | 0.35 | 0.75 | 0.9 | 0.8 | 0.7 |
| | 4/18/89 | 0.95 | 0.5 | 0.3 | 0.35 | 0.7 | 0.85 | 0.75 | 0.7 |

FIGURE 1
AGEING KINETICS AT 120°C IN OXYGEN

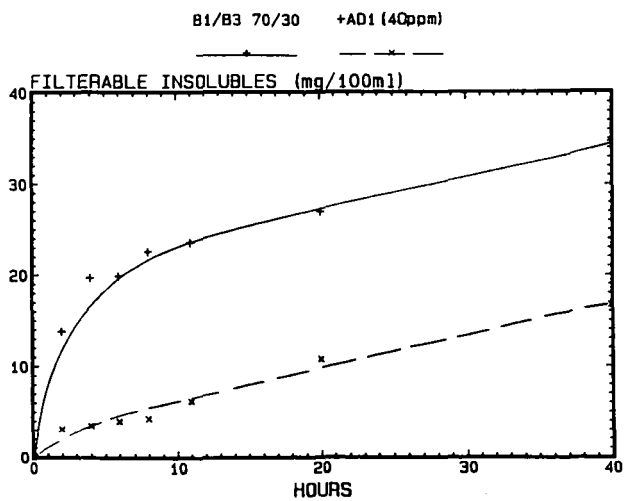
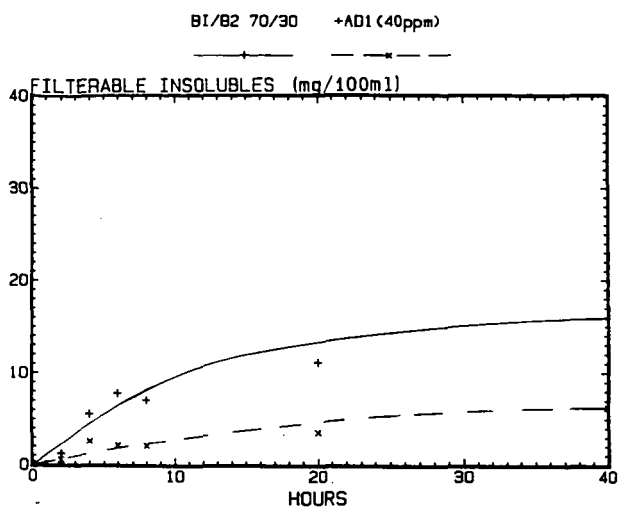


FIGURE 2
AGEING KINETICS AT 43°C IN AIR (WITHOUT ADDITIVES)

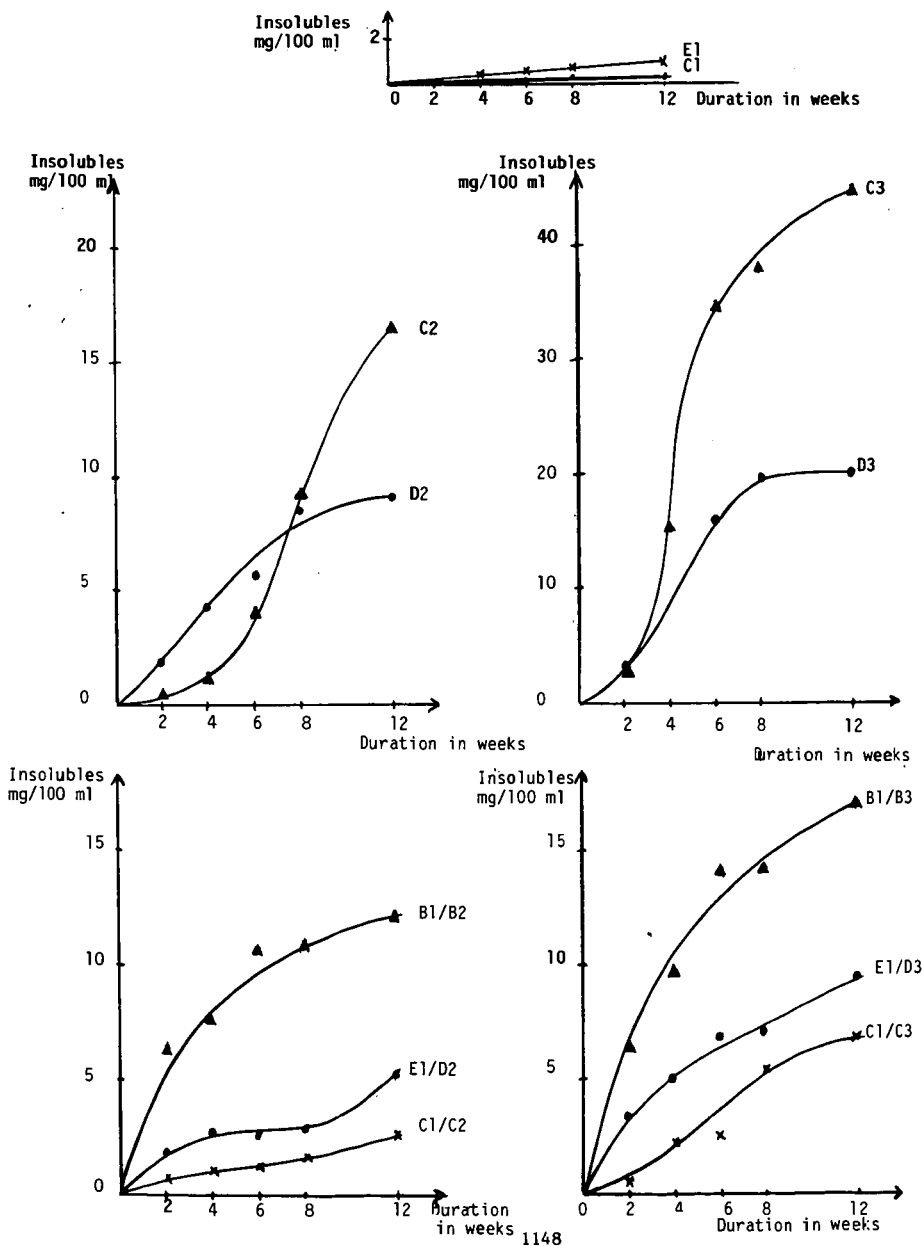


FIGURE 3

AGEING KINETICS AT 43°C IN AIR (WITH ADDITIVES)

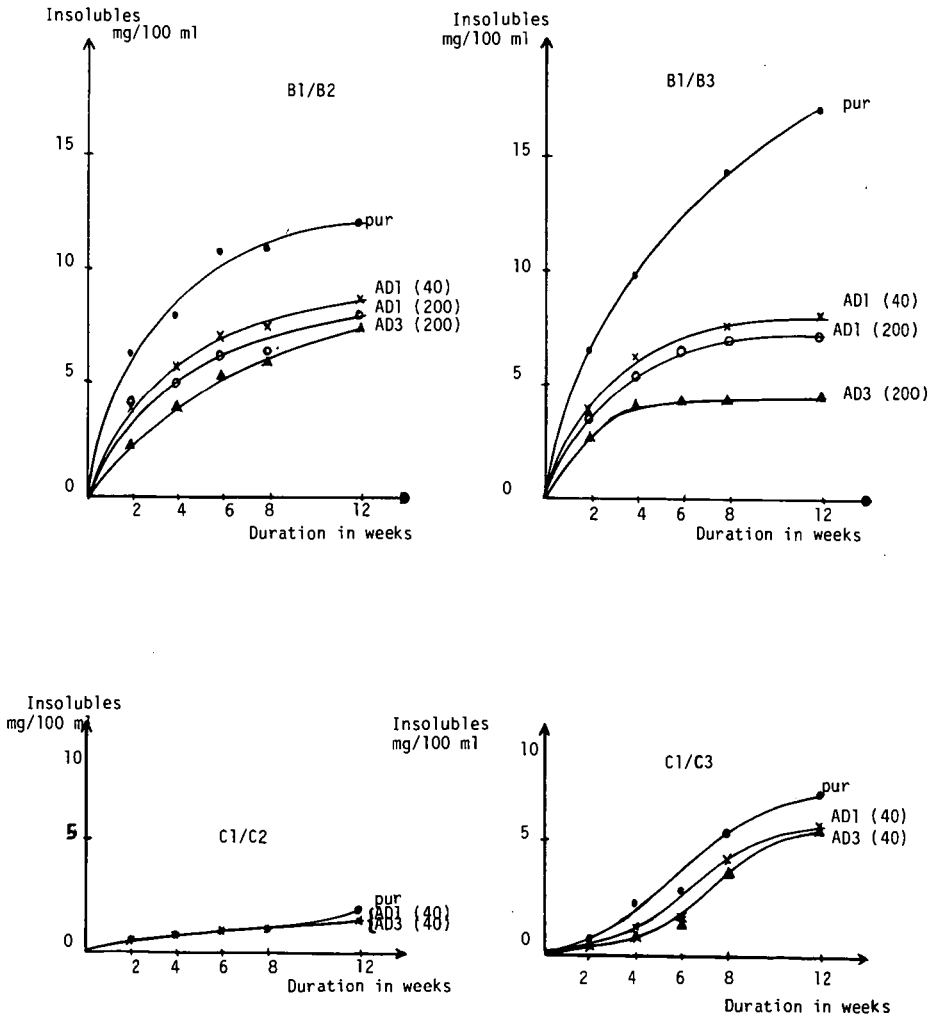


FIGURE 4
NPD CHROMATOGRAM OF NITROGEN COMPOUNDS IDENTIFIED IN A LCO

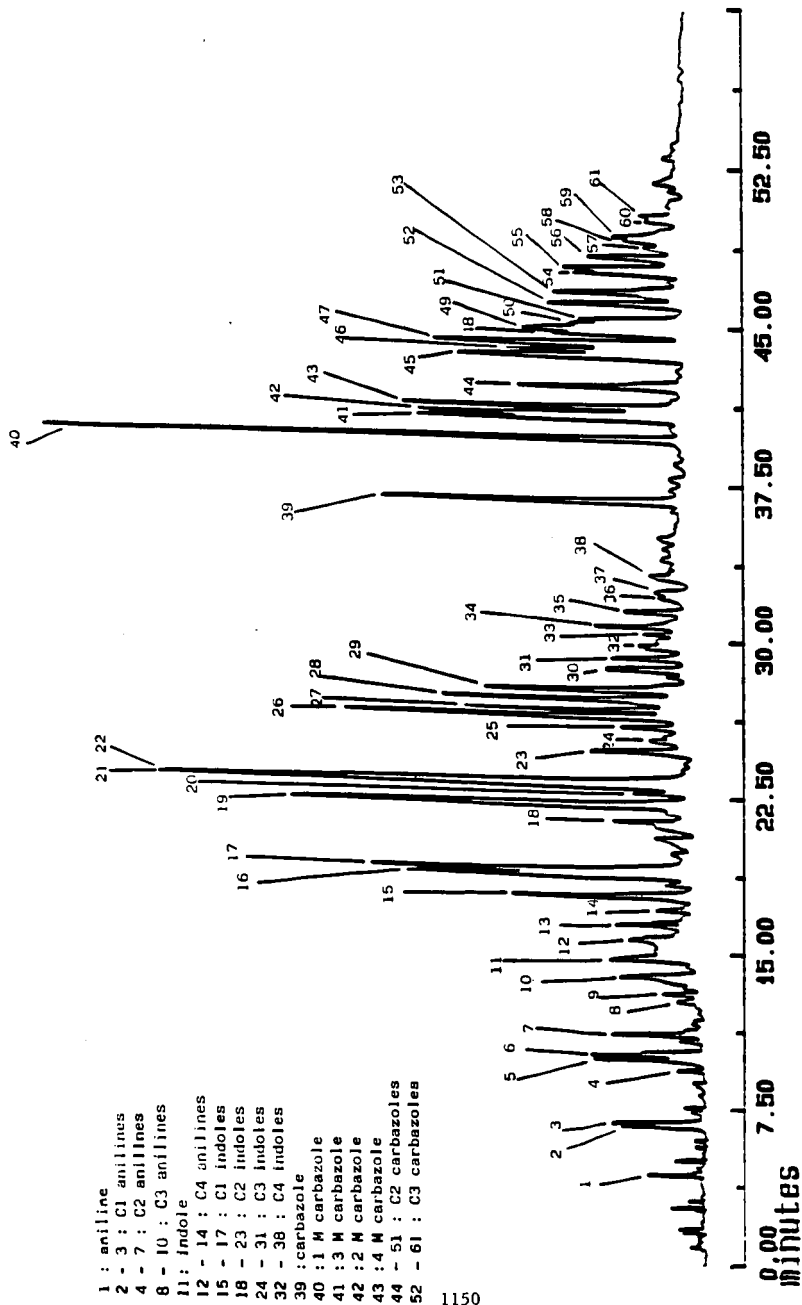
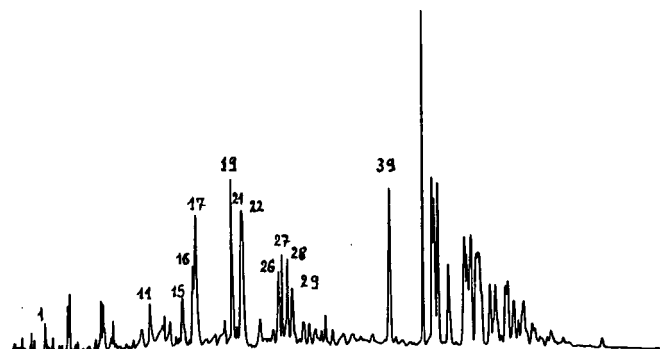
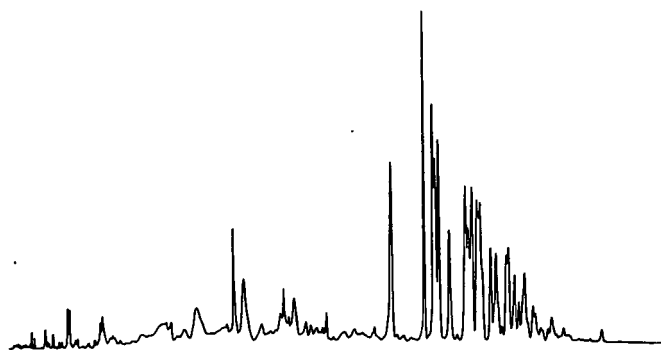


FIGURE 5
 NPD CHROMATOGRAMS OF LCO B2, BEFORE AGEING, AFTER AGEING AT 43°C,
 AND AFTER AGEING AT 120°C

LCO B2



LCO B2
 12 WEEKS AT 43°C



LCO B2
 8 HOURS AT 120°C

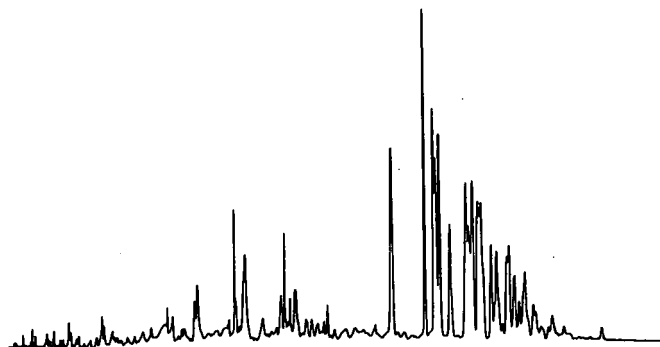


FIGURE 6
NITROGEN COMPOUNDS AS A FUNCTION OF TIME AT 120°C

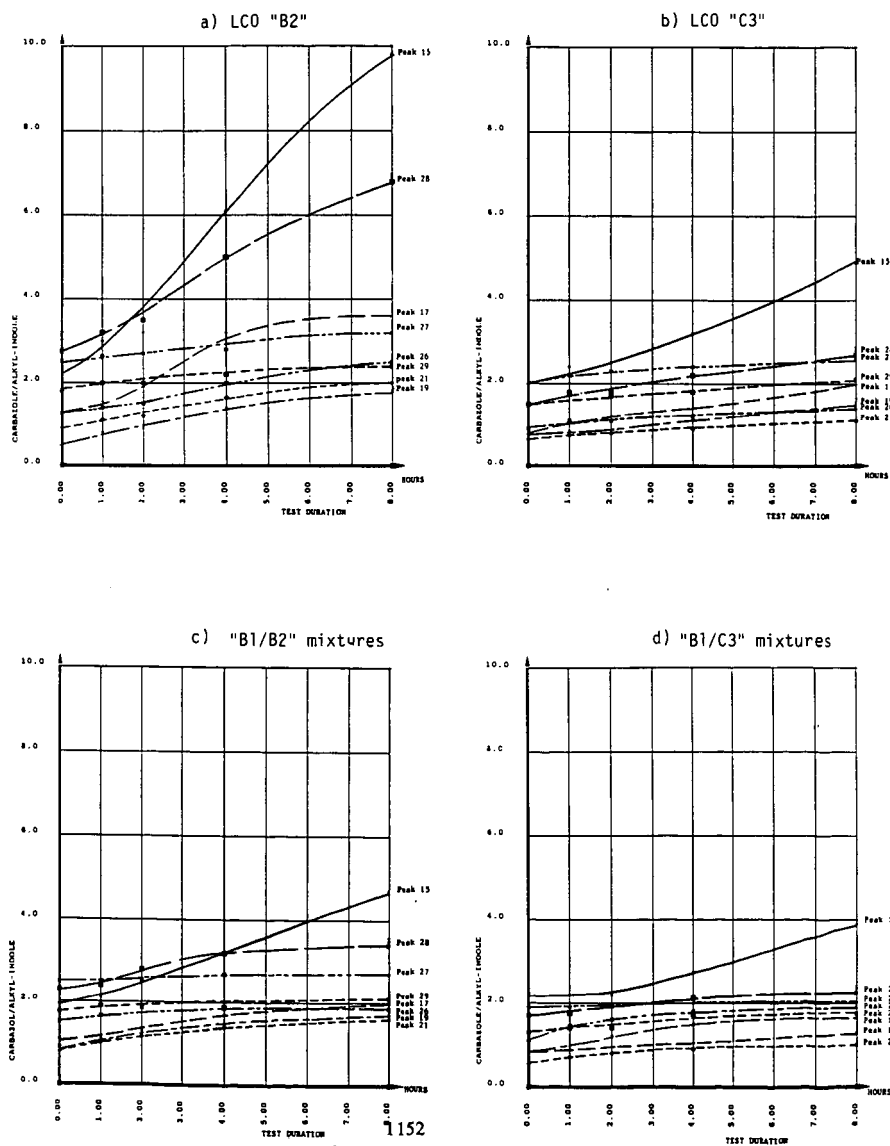


FIGURE 7
NITROGEN COMPOUNDS AS A FUNCTION OF TIME AT 43°C

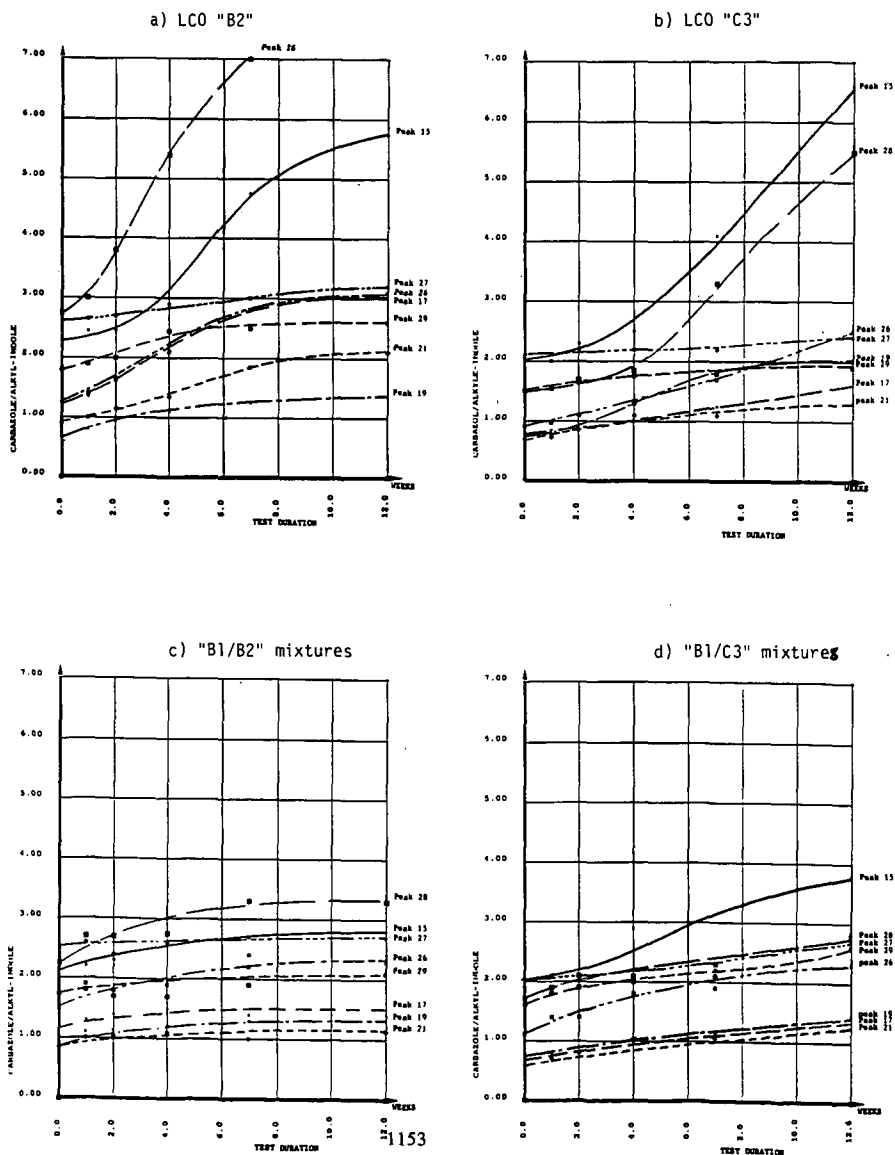


FIGURE 8
INFLUENCE OF ADDITIVES ON CHANGES IN NITROGEN COMPOUNDS IN B1/B3 70/30 MIXTURES
SUBJECTED TO AGEINGS

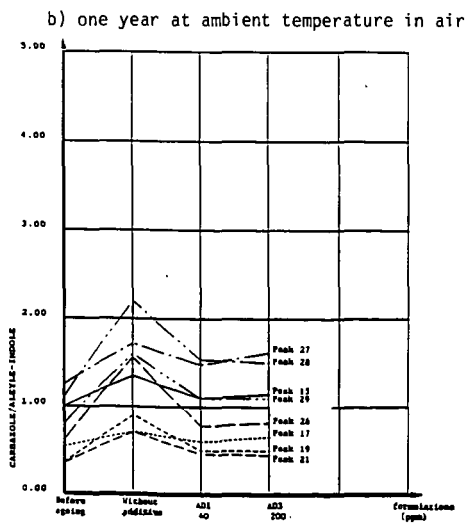
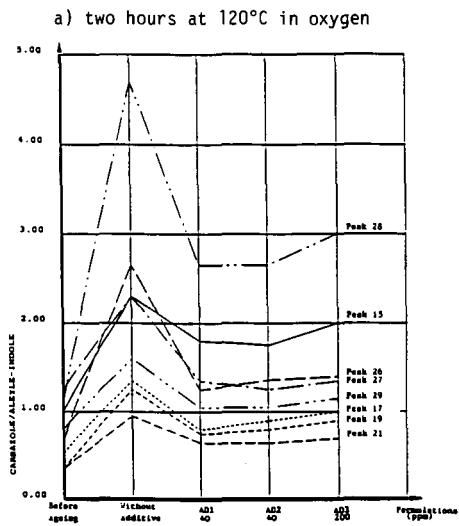


FIGURE 9

INFLUENCE OF ADDITIVES ON CHANGES IN NITROGEN COMPOUNDS IN C1/C3 70/30 MIXTURES
SUBJECTED TO AGEINGS

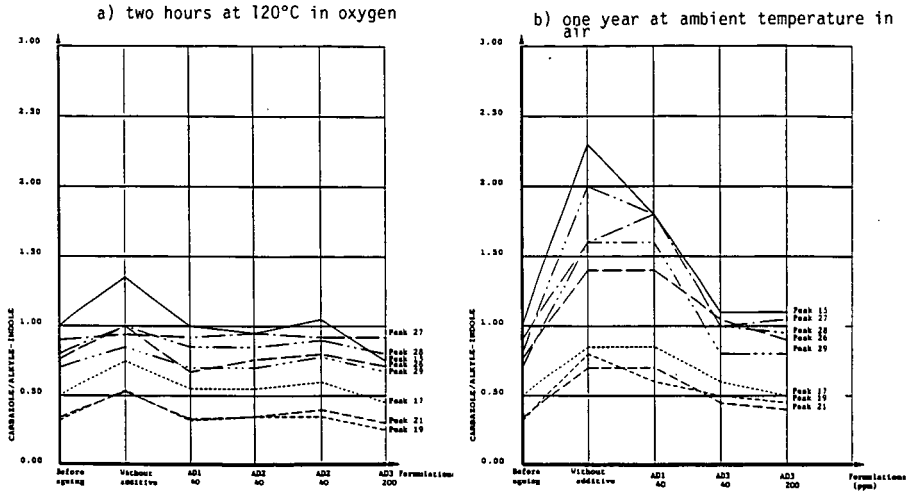


FIGURE 10

INFLUENCE OF ADDITIVES ON CHANGES IN NITROGEN COMPOUNDS IN C1/C2 70/30 MIXTURES
SUBJECTED TO AGEINGS

